Organic Chemistry

SECOND EDITION

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NEW YORK

In summary, the hydroxy group in COOH can be replaced by halogen by using the same reagents employed in the conversion of alcohols into haloalkanes—$SOCl_2$ and PBr_3. The resulting alkanoyl (acyl) halides are sufficiently reactive to be attacked by carboxylic acids to generate carboxylic anhydrides. Cyclic examples of the latter may be made from dicarboxylic acids by thermal dehydration.

19-9 Carboxylic Acid Derivatives: Esters

Esters have the general formula $R\overset{O}{\overset{\|}{C}}OR'$. They are perhaps the most important of the carboxylic acid derivatives. This section describes two methods by which esters are made—the mineral acid-catalyzed reaction of carboxylic acids with alcohols and the synthesis of methyl esters using diazomethane.

Carboxylic acids react with alcohols to form esters

When a carboxylic acid and an alcohol are mixed together, no reaction takes place. However, upon addition of catalytic amounts of a mineral acid, such as sulfuric acid or HCl, the two components combine in an equilibrium process to give an ester and water (Section 9-4).

Acid-Catalyzed Esterification

$$\underset{\text{Carboxylic acid}}{R\overset{O}{\overset{\|}{C}}OH} + \underset{\text{Alcohol}}{R'OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R\overset{O}{\overset{\|}{C}}OR'} + H_2O$$

Esterification is not very exothermic. How can the equilibrium be shifted toward the ester product? One way is to use an excess of either of the two starting materials; another is to remove the ester or the water product from the reaction mixture. In practice, esterifications are most often accomplished by using the alcohol as a solvent.

$$\underset{\text{Acetic acid}}{CH_3\overset{O}{\overset{\|}{C}}OH} + \underset{\text{Solvent}}{CH_3OH} \xrightleftharpoons{H_2SO_4,\ \Delta} \underset{\text{Methyl acetate}}{CH_3\overset{O}{\overset{\|}{C}}OCH_3} + H_2O \qquad 85\%$$

The opposite of esterification is **ester hydrolysis.** This reaction is carried out under the same conditions as esterification, but, to shift the equilibrium, an excess of water is used in a water-miscible solvent.

$$\underset{\text{Ethyl 2,2-dimethylhexanoate}}{CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}COOCH_2CH_3} \xrightarrow{H_2SO_4,\ HOH,\ \text{propanone (acetone)},\ \Delta} \underset{\text{2,2-Dimethylhexanoic acid}}{CH_3CH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}COOH} + CH_3CH_2OH \qquad 85\%$$